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PATENT APPLICATION
Docket No. 16785.1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:		)
Applicant:	SCHERMANZ ET AL.	)
Title:	EXHAUST GAS CATALYST COMPOSITION	) Art Unit) 4181
Serial No.:	10/595,795	)
Filed:	August 15, 2006	)
Confirmation No.:	6850	)
Examiner:	DARJI, PRITESH D	)

DECLARATION OF DR. KARL SCHERMANZ UNDER 37 C.F.R. & 1.132

Mail Stop AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I hereby declare as follows:

1. I am personally knowledgeable of the facts stated herein.

2. I am an inventor of U.S. Patent Application Serial No. 10/595,795 ("Subject Application"), and thereby have a personal interest in the Subject Application.

3. I have significant experience in the art of NOx catalysts and method of preparation as applied in the Subject Application which is currently under examination. (*see* Appendix A: Curriculum Vitae of Dr. Karl Schermanz).

4. I have read and agree with the information found in the Evidentiary Appendix B executed by Prof. Alessandro Trovarelli, provided herewith.

5. I have reviewed and understand the Subject Application and the Inoue and Wu references.

6. I have reviewed the response to the Office Action being filed herewith, and attest that the claimed process for preparing a NOx catalyst resulted in surprising and unexpected results in that use REVanadates in preparing a NOx catalyst can provide temperature stability and the ability to retain a high catalytic activity even after being aged at a temperature of as high as 750°C. Previously, all vanadium based catalysts of the prior art are based on V2O5 oxides as the active component. That means that these catalysts begin to sinter from 650°C on and are melting at 690°C, due to their melting behaviour. Accordingly, a deactivation of the catalyst occurs (See Jan MT et al., Chemical Engineering & Technology, Vol. 30, Nr. 10, 1440-1444, 2007).

7. I attest asserts that claims 21 and 22 are patentable over the art of record and these claims will be granted by the EPO in the corresponding EP application number EP20040797861.

8. I attest that the presently claimed invention is a process that surprisingly and unexpectedly can use REVanadates in preparing a NOx catalyst with temperature stability and the ability to retain a high catalytic activity even after being aged at a temperature of as high as 750°C. The prior art used a mixture of RE and vanadium oxides to prepare catalysts that sintered and melted at temperatures lower than 750°C, which results in lowered catalytic activity. Thus, the use of REVanadates instead of a mixture of RE and vanadium oxides provides the surprising and unexpected results of temperature stability and retention of high catalytic activity even after exposure to temperatures as high as 750°C, and the claimed process and resulting NOx catalyst should be considered to be novel and inventive because the catalysts described in Inoue cannot exhibit the thermal stability of the claimed catalysts because of the low sintering and melting temperature of V2O5.

9. I attest that Comparative Example 1 of Appendix C herein demonstrates that even very low concentrations of rare earth vanadate present as a dopant do show the catalytic effect. The

concentrations of dopant applied corresponds to V contents less than 0.05 % in the catalyst. As can be seen, the catalyst is effective even when the content of the rare earth vanadate is close to zero.

10. I attest that the catalyst examples based on REVanadates (e.g., Table 2b of the application) prepared according to the claimed process of claims 21 and 23 of the present application show good efficiency and high activity, even after exposure to elevated temperatures that would sinter and/or melt catalysts having V2O5.

11. I attest that Comparative Example 2 of Appendix C demonstrates that the technical effect of the invention (e.g., thermal stability of the catalyst) is effectively associated with the presence of rare earth vanadate (e.g., REVO4). Catalysts doped with transition metal based vanadates do loose significant activity after ageing. In contrast, catalysts doped with rare earth vanadates do show an increase of catalytic activity after ageing at 700°C/10 hrs and even more pronounced at 750°C/10 hrs. Such a result is surprising and unexpected.

12. I attest that Comparative Example 3 of the Experimental Report is submitted to demonstrate that no rare earth vanadates are produced in the process disclosed in US 4,466,947 (cited in the International Search Report). Therefore, the claimed invention is novel and inventive.

13. I declare further that all statements made herein of our own knowledge are true and that all statements are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful, false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 6th day of November, 2009.

Dr. Karl Schermanz

Dr. Karl Schermanz

APPENDIX A

CURRICULUM VITAE

Personal data:

Name:	Karl Schermanz
Born:	September 30, 1954 in Klagenfurt, Austria
Nationality:	Austrian
Marital status:	Married

Education and academic degrees:

1972	(23.06.) **Abitur (Matura)** 2. Bundesgymnasium, Klagenfurt, Austria
1979	**Magister Pharmaciae** (Mag. pharm.), University of Graz, Austria
1983	**Doctor rerum naturalium (Dr. rer. nat.)** in pharmaceutical chemistry, University of Graz (with distinction "summa cum laude")

Training courses with relevance to automotive exhaust gas after treatment:

4. FAD Conference, Dresden 2006
SCR-System, Car Training Institute, Forum 9 – 10 May 2007, Stuttgart (Germany)
SCR-System, Seminar 8 – 10 April 2008, Bonn (Germany)

Regular academic positions:

01.01.1980 - 31.12.1983	Scientific Assistant, Institute of Pharmaceutical Chemistry, University of Graz (chair Prof. Dr. G. Zigeuner)
01.01.1984 - 30.09.1989	Research Chemist at chemical company "CHEMIE LINZ AG", Linz , Austria
Since 01.10.1989	**Employee of Treibacher Industrie AG and in its subsiduary "Treibacher Auermet "in different positions:**
1989 - 1990	Head of R&D department "Chemical process development"
1991 -1994/6	Head of R&D department „Rare Earth Chemistry"

1994/7 – 1996	Plant Manager of „Rare Earth" in Treibacher Auermet
1997 – 2002/6	Head of R&D in Treibacher Auermet
Since 2002/7	Head of R&D department "Rare Earth Chemistry" in Treibacher Industrie AG

Research experience:

- Organic chemistry:
  Synthesis of active ingredients applicable as pharmaceuticals and phytopharmaceuticals (at University Graz and Chemie Linz)
- **Inorganic Chemistry with emphasize on Rare Earths**:
  Synthesis of mainly functional materials based on Rare Earths and Vanadium for application in the fields of **catalysis**, glass and ceramics, pharmaceuticals.

Overview on Publications

Organic Chemistry

More than 30 patents, patent applications and scientific papers in synthesis of organic materials (out of work at University Graz and Chemie Linz)

Inorganic Chemistry

Several patents and patent applications in fields of Rare Earths

Publications with relevance to Rare Earths and Catalyst Applications:

Articles, Scientific Books:

Seltene Erden (Rare Earths)
Herfried Richter, **Karl Schermanz**
Aktualisierung des Beitrags aus der 4. Auflage (actualisation of chapter Rare Earths) in
Winnacker-Küchler: Chemische Technik
Prozesse und Produkte. Band 6B: Metalle
Winnacker, Chemische Technik (Volume 6b)

Co-Autor of **„Catalysis by Ceria and Related Materials"** (edited by A. Trovarelli) Imperial College Press, 2002;

Publications

M. Casanova, A. Trovarelli, Università di Udine/I; **K. Schermanz, Treibacher Industrie,** Althofen/A; I. Begsteiger, Frauental GmbH, Frauental/A **"Activity and high-temperature stability of SCR catalysts modified with rare-earths" 4th International Conference on Environmental Catalysis (Heidelberg, 2005)**
K. Schermanz, Treibacher Industrie AG, „High-temperature Stability of SCR Catalysts Modified with Rare –earths Rare Earth 04; Nara , Japan 2004

APPENDIX B

The influence of Tungsten on SCR activity in a TiO2-Rare Earth-V- System

I, Prof. Alessandro Trovarelli, one of the inventors of WO 2005/046864, declare that I have undertaken the following experiments showing the significant influence of tungsten in the TiO2-RE-Vanadate system on NOx conversion. For this there were compared 2 tungsten free and 2 tungsten containing materials based on TiO2-RE-Vanadates (RE being Er and Tb).

A) Preparation of the Tungsten free materials:

Preparation of TiO2/ 8.41% $ErVO_4$

104.6 mg of ammonium metavanadate were dissolved in 15 ml of oxalic acid 1N. The solution was heated in order to obtain the blue complex $(NH_4)_2[VO(C_2O_4)_2]$ and then 3717.17 mg of Er-acetate solution were added. Moreover, some drops of HNO_3 were added in order to avoid the precipitation of the terbium oxalate. Then, the support [2747.7 mg of TiO_2 (DT 51)] was added. This slurry was brought to dryness under continuous stirring at 80-100°C. Finally, the solid was dried at 120°C overnight and calcined at 650°C for 2 hours, pressed into pellets, crushed and sieved in the range 355-425 µm. Ageing of the sample was carried out in a tubular furnace at a temperature of 750°C for 10 h under air.

Preparation of TiO2/ 8.41% $TbVO_4$

107.7 mg of ammonium metavanadate were dissolved in 15 ml of oxalic acid 1N. The solution was heated in order to obtain the blue complex $(NH_4)_2[VO(C_2O_4)_2]$ and then 417.3 mg of $Tb(NO_3)_3 \cdot 6H_2O$ were added. Moreover, some drops of HNO_3 were added in order to avoid the precipitation of the terbium oxalate. Then, the support [2747.7 mg of TiO_2 (DT 51)] was added. This slurry was brought to dryness under continuous stirring at 80-100°C. Finally, the solid was dried at 120°C overnight and calcined at 650°C for 2 hours, pressed into pellets, crushed and sieved in the range 355-425 µm. Ageing of the sample was carried out in a tubular furnace at a temperature of 750°C for 10 h under air.

B) Preparation of Tungsten containing materials:

Preparation of TiO2/WO3/ 8.41% $ErVO_4$ (corresponds to 5 % Er and 1.5 % V)
This material was prepared accoding to example 17 of WO 05/046864.

Preparation of TiO2/ 8.41% $TbVO_4$
This material was prepared accoding to example 18 of WO 05/046864.

Catalyst testing was carried out in the apparatus described in WO 05/046864. The gas feed consisted of NH_3/N_2, NO/N_2, O_2, N_2. Mass flow meters were used to measure and control the single gaseous stream while an injection pump was used to introduce water. The feed stream was preheated and premixed and ammonia was added to the gaseous mixture immediately before entering the reactor to avoid side reactions. A tubular quartz reactor was employed inserted in a furnace. Temperature was controlled by a thermocouple inserted in the catalyst bed. The gas exiting the reactor was scrubbed with an aqueous solution of phosphoric acid to trap unconverted ammonia and then cooled to condense water vapor. Activity of the catalysts were measured under stationary conditions in a temperature range of 250°C to 450°C. Unless otherwise reported the standard gas composition and reaction conditions given in Table 1 were used. Conditions were selected in order to have a conversion not exceeding ca. 90% with reference catalyst. Gas composition analysis was carried out with an FTIR spectrometer equipped with a gas cell.

Results and conclusion:

The tungsten free catalysts show significant lower activity and particularly a drop in catalytic activity after thermal treatments, in contrast to what was found for the WO3 containing materials (compare examples 17, 17a and 18, 18a in table 2 and Table 3).

These results clearly show that WO_3 plays a significant role in increasing the activity and thermal stability of these catalysts.

Table 1: Reaction conditions and gas composition.

Catalyst weight	100,0 mg
Particle size	350-425 µm
Total flow	0,3 l/min
Temperature	250-450°C
NO conc.	200 ppm
NH3 conc.	240 ppm
O2 conc.	20000 ppm
H2O conc.	10%
N2 conc.	balance

Table 2: Activity (NOx conversion in %) of tungsten free catalysts, fresh and aged catalysts containing RE and V and TiO_2.

Example Nr	RE	RE [%]	V [%]	250°C fresh	320°C fresh	450°C fresh	250°C aged	320°C aged	450°C aged
17a	Er	4,6	1,7	31	66	20	0	9	6
18a	Tb	4,6	1,7	28	60	21	10	21	0

Table 3: Activity (NOx conversion in %) of tungsten containing catalysts, fresh and aged catalysts containing RE and V and WO_3 and TiO_2 (WO_3 : TiO_2 =10:90).

Example Nr	RE	RE [%]	V [%]	250°C fresh	320°C fresh	450°C fresh	250°C aged	320°C aged	450°C aged
17	Er	4,6	1,7	58	81	46	17	46	9
18	Tb	4,6	1,7	62	88	48	25	48	29

Prof. Alessandro Trovarelli

APPENDIX C

EXPERIMENTAL REPORT

Comparative Example 1

Determination of catalytic activity of $TiO_2/WO_3/SiO_2$ doped with low concentrations of $ErVO_4$ (after heat treatment 750°C/10 hrs).

Preparation of the catalyst:
2 Catalysts (A and B) were prepared according to the description disclosed under 1.4.2. in WO 2005/046864 using $TiO_2/WO_3/SiO_2$ as a support material by introducing different amounts of $ErVO_4$ as a dopant.
The amounts of $ErVO_4$, Er and V in the prepared catalyst are listed in table 1.
The catalytic activity of the samples was measured after applying ageing procedure (750°C/ 10 hrs) according to the test disclosed under 3. in WO 2005/046864, results shown in table 2.

Table 1 (Amounts of dopant in catalyst)

Catalyst	$ErVO_4$ [%]	Er [%]	V [%]
A	0,84	0,50	0,15
B	0,2	0,12	0,03

Table 2, Catalytic activity (NO conversion in %) at different temp. of aged catalysts (750°C/ 10 hrs)

Catalyst	NO conversion in % at 250°	NO conversion in % at 320°	NO conversion in % at 450°
A	29	66	52
B	7	58	42

Conclusion:
Even very low concentrations of $ErVO_4$ present as a dopant do show a catalytic effect ! The concentrations of dopant applied corresponds to V contents less than 0,05 % in the catalyst.

Comparative Example 2

Comparison of Catalytic Activity of "Rare Earth Vanadate" containing catalyst versus "Transition Metal Vanadate" containing Catalyst

Objective: Proof on effect of Rare Earths contributing to thermal stability of catalyst in the TiO2/WO3/SiO2 system.

For the experiments 3 different types of dopants were used to show the effect of Rare earths on activity of the catalyst after ageing. All the 3 dopants themselves are thermally stable up to temp. > 800°C

Dopants used for making the catalyst:

a) ErVO4 (Rare Earth Vanadate)
b) FeVO4 (Transition Metal Vanadate)
c) MnV2O7 (Transition Metal Vanadate)

2.1. Preparation of ErVO4 and Transition Metal Vanadates

2.1.1. Preparation of ErVO4
ErVO4 was prepared according to the description disclosed in WO2005/46864 under 1.4.1.

2.1.2. Preparation of Fe-Vanadate
119,7 g Fe(III)(NO3)3 x 9 H2O (Fe2O3 content = 19,5 %) was dissolved in approx. 320 ml water to yield a solution. On the other hand 34,3 g ammonium metavanadate (V2O5 content = 77,6 %) was dissolved in approx. 1100 ml water at approx. 80°C. After mixing the solutions under continous stirring the pH was adjusted tom 7,25 by adding 24% ammonia solution. The slurry with precipitate so formed was stirred for ½ hr, filtered, the precipitate washed several time with deionised water and dryed at 120°C to yield Fe-Vanadate (FeVO4), structure proved by elemental analysis and XRD spectra.

For FeVO4 there is reported a melting point of 880°C by SHUBHA GUPTA et al. in J. of Material Sciences Letters, Vol 5, number 5, July 1986

2.1.3. Preparation of Mn-Vanadate
Mn-Vanadate was prepared according to the description disclosed under 2.1.1 using 66,4 g of Mn(II)(NO3)2 * 6 H2O (MnO2 content = 34,6 %) and 34,3 g ammonium metavanadate (V2O5 content = 77,6 %). After filtration, washing and drying of the precipitate there was yielded Mn-Vanadate (structure according to XRD being Mn2V2O7).
Remark: Since Mn is present as an (+2) Ion in the starting material Mn(NO3)2 a formula of MnVO4 cannot exist. The synthesized Mn-Vanadate corresponds therefore to the structure

Mn2V2O7 as proved by XRD. However, oxidation stage of Vanadium in the compound is +5 (like in Rare Earth Vanadates (REVO4) and in FeVO4).

For Mn2V2O7 there is reported a melting point of 820°C by Park et al. in US Patent 6 777 363.

2.2. Preparation of the catalysts and measurement of catalytic activity.

3 Catalysts (A -C) were prepared according to the description disclosed under 1.4.2. in WO 2005/046864 using TiO2/WO3/SiO2 as a support material by introducing the dopants ErVO4 (Catalyst A), FeVO4 (Catalyst B) and Mn2V2O7 (Catalyst C).

Thus 252,3 mg of the "Metal Vanadate"(Er, Fe and Mn) and 2747,7 mg of the TiO2/WO3/SiO2 support material were used for preparing the catalyst.
Ageing of the catalyst was performed at 700°C/10 hrs and 750°C/ 10 hrs respectiveley.

The catalytic activity of the "fresh" and "aged" samples were measured according to the test disclosed under 3. in WO 2005/046864, results shown in table 3.

Table 3

Sample	Dopant	Ageing conditions [°C/hrs]	% NO conversion at 250°C	% NO conversion at 270°C	% NO conversion at 300°C	% NO conversion at 320°C	% NO conversion at 450°C
Example 18, WO 2005/046864	ErVO4	Fresh 750 /10	33 73	na	na	75 91	64 46
Catalyst A	ErVO4	Fresh 700 / 10	25 56	na 70	70 82	na	na
Catalyst B	FeVO4	Fresh 700 / 10	72 19	88 28	93 39	na	na
Catalyst C	Mn2V2O7	Fresh 700 / 10 750 / 10	27 1 0	42 2 na	60 2 na	na 0	na 0

Conclusion:
The examples clearly demonstrate the contribution of Rare Earths to the thermal stability of the catalyst. Catalysts doped with transition Metal based Vanadates do loose significantly their activity after ageing; in contrast catalysts doped with Rare Earth Vanadates do show an increase of catalytic activity after ageing at 700°C/10 hrs and even more pronounced at 750°C/10 hrs.

Comparative Example 3

No Formation of Rare Earth Vanadates in view of D5 (US 4 466 947)

To proof about non formation of RE-Vanadate in an example which was made according to example 1 disclosed in US 4 466 947.

There was made an experiment using the basics of example 1 of US 4 466 947 additionally introducing Er2O3 into the system.

Thus 25,3 g of Titanic Acid (containing 87,2 % TiO2) where suspended in approx. 100 ml of water yielding a supension with a pH value of 4,9. The suspension was neutralized with aquous ammonia to reach a pH of 7,02. 1,55 g Erbiumoxide (Er2O3) was added under stirring to the suspension.

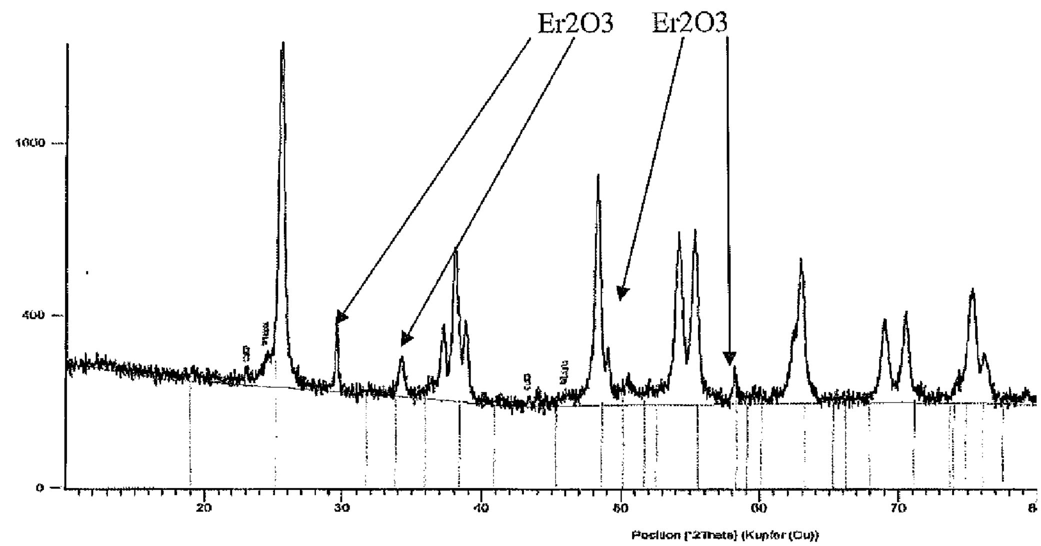
1,86 g Ammoniumparatungstate (containing 88,7 % WO3) was dissolved in approx. 50 ml of hot water and the solution added to the Ti/Er-mixture. The water was evaporated until the material could be pressed. A tablet (diameter approx. 2,5 cm) was formed by using a press.

The tablet was dried at 80°C for 12hrs and calcined at 500°C for 5 hrs. Afterwards the tablet was dipped into a bath of monoethanolamine and dried. Finally the tablet was dipped into a solution of Vanadayloxalate containing 4,2 % of V2O5 dried and calcined at 750°C for 10 hrs.
After calcination the sample was crushed and the resulting powder subjected to XRD analysis.
No peaks for ErVO4 could be detected in the XRD spectra of the sample.

Attachments:
Graph 1 - XRD-Spectrum of sample
Peaks for ErVO4 (not being present) marked by vertical lines; Er2O3 peaks marked by “arrows”; other (not marked peaks) relate to TiO2.

Graph 2 – XRD Spectrum of ErVO4

Graph 1 - Sample



Graph 2 – ErVO4